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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> :  C07C 17/38, 19/08	A1	(11) International Publication Number: WO 94/25419  (43) International Publication Date: 10 November 1994 (10.11.94)
(21) International Application Number: PCT/US94/04301		(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 25 April 1994 (25.04.94)		
(30) Priority Data: 08/055,486 30 April 1993 (30.04.93) US 08/208,256 9 March 1994 (09.03.94) US		Published <i>With international search report.</i>
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(54) Title: AZEOTROPIC AND AZEOTROPE-LIKE COMPOSITIONS AND A PROCESS FOR SEPARATING HCl AND HALOCARBONS		
(57) Abstract		The present invention discloses azeotropic or azeotrope-like compositions which include HCl that can be employed in a distillation or an extractive distillation process for separating HCl from pentafluoroethane, chloropentafluoroethane, chlorotrifluoroethane, trifluoromethane, and other fully saturated and unsaturated fluorocarbons, chlorofluorocarbons and chlorocarbons.

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TITLE5      AZEOTROPIC AND AZEOTROPE-LIKE COMPOSITIONS AND A  
PROCESS FOR SEPARATING HCl AND HALOCARBONSCross-Reference to Related Patent Application

This Application is a continuation in part of U.S. Patent Application Serial No. 08/055,486, filed on April 30, 1993, in the names of Barry A. Mahler et 10 al., and entitled "Process For Separating HCl and Halocarbons"; the entire disclosure of which is hereby incorporated by reference.

Field Of The Invention

The present invention relates to the field of separating HCl from a 15 mixture comprising HCl and one or more halocarbons.

Background Of The Invention

Hydrofluorocarbons (HFCs), such as pentafluoroethane (HFC-125), are non-chlorine containing fluorocarbons that can be used as a refrigerant, blowing 20 agent, propellant, fire extinguishing agent, sterilant carrier gas, among other valuable uses. By being non-chlorine containing, HFCs are believed to have less effects upon the earth's ozone layer.

One method for making pentafluoroethane comprises chlorofluorinating perchloroethylene to produce a mixture comprising trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114), and dichlorotrifluoroethane (HCFC-123), along with by-product HCl. After removing at least some HCl and trichlorotrifluoroethane, the remaining mixture can be fluorinated by various processes thereby producing a mixture containing pentafluoroethane (HFC-125), chloropentafluoroethane (CFC-115), by-product HCl and lesser amounts of 30 other fluorinated and chlorinated compounds, e.g., chlorotrifluoromethane (CFC-13) and trifluoromethane (HFC-23).

Certain halocarbons have been separated using conventional distillation. Another distillation method relates to extractive distillation. Procedures which have been used for predicting what extractive agents are likely to be effective in a given separation method have been described by L. Berg in an article published 35 by Chem. Eng. Progress, Vol. 65, No. 9, pages 52-57, Sept. 1969; the contents of

which are hereby incorporated by reference. In discussing extractive distillation, it was stated in the previously identified article that "...hydrogen bonds appear to be an important factor since all successful extractive distillation agents are highly hydrogen bonded liquids. Thus, the criteria for successful extractive agents are that they boil 5 considerably higher than the compounds being separated, form no minimum azeotropes with the components, and be a highly hydrogen bonded liquid, that is, Class I or Class II of the hydrogen bond classification. Phenols, aromatic amines (aniline and its derivatives), higher alcohols, glycols, etc. are examples of successful extractive agents."

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#### Summary Of The Invention

The economic feasibility of a process for manufacturing certain halocarbons is dependent upon obtaining a useful HCl by-product. HCl is used in the pharmaceutical and food product industries. However, the utility of HCl in such 15 industries typically requires that the residual halocarbon quantity be relatively low, e.g., typically less than about 100 ppm by weight of halocarbon in the HCl. Conventional distillation processes have been unable to obtain HCl product which is substantially free from halocarbons. By substantially free from halocarbons it is meant that the HCl product contains less than about 100 ppm by weight halocarbon.

20 Normally, the substantially halocarbon free HCl product is anhydrous, e.g., containing less than about 100 ppm water.

The present invention solves the problems associated with conventional distillation processes, and relates to an extractive distillation process for separating HCl from one or more halocarbons such as pentafluoroethane, 25 chloropentafluoroethane, chlorotrifluoromethane, trifluoromethane and other fully saturated and unsaturated fluorocarbons, and/or chlorocarbons, all optionally containing hydrogen. The extractive distillation process of the invention employs certain compounds or extractive agents that are not highly hydrogen bonded. By "not highly hydrogen bonded" it is meant that the extractive agents are not 30 characterized as being Class I or Class II of the hydrogen bond classification.

The present invention provides a method of removing halocarbons from HCl wherein the halocarbons comprise at least one member selected from the group of saturated fluorocarbons, saturated and unsaturated hydrofluorocarbons, saturated and unsaturated hydrochlorofluorocarbons, saturated and unsaturated 35 chlorofluorocarbons, saturated and unsaturated hydrochlorocarbons, saturated and unsaturated chlorocarbons, among others.

One aspect of the present invention relates to a process for separating HCl from a first mixture of HCl and at least one member from the group of pentafluoroethane, chloropentafluoroethane, chlorotrifluoromethane, trifluoromethane, among others. The process comprises the steps of:

- 5 adding a fluorocarbon, chlorofluorocarbon or chlorocarbon extractive agent having 1 to 5 carbon atoms, either saturated or unsaturated, optionally including hydrogen; and having a boiling point at atmospheric pressure typically greater than about -48°C, normally greater than about -15°C, and less than about 120°C, usually less than about 80°C, to the first mixture in order to form a second mixture,
- 10 separating HCl from the halocarbons in the second mixture by extractively distilling the second mixture in an extractive distillation zone, and recovering HCl as an overhead product which is substantially free from the halocarbons of the first mixture.

In addition to being not highly hydrogen bonded, the extractive agent used in the present invention can be related chemically to the halocarbon which is being separated from the HCl. By "chemically related" it is meant that the extractive agent comprises a halocarbon optionally containing hydrogen. Examples of such related extractive agents comprise one or more compounds having 1 - 5 carbons atoms and which include hydrogen and/or fluorine and/or chlorine atoms.

- 20 Using a chemically related extracting agent typically minimizes the risk of introducing extraneous impurities into the halocarbons being separated.

Representative extractive agents suitable for use in the present invention comprise one or more saturated or unsaturated C1 through C5 compounds such as fluorocarbons, chlorofluorocarbons, or chlorocarbons, each optionally containing hydrogen, among others. Specific examples of suitable extractive agents comprise or consist essentially of at least one member selected from the group of 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), 2,2-dichloro-1,1,1,2-tetrafluoroethane (CFC-114a), 1,1,1,2,2-pentafluoroethane (HFC-125), 1-chloro-1,1,2,2,2-pentafluoroethane (CFC-115), their isomers, mixtures thereof, among others.

Another aspect of the invention relates to azeotropic and azeotrope-like compositions that can form between a mixture consisting essentially of at least two members from the group of HCl, CFC-13, HFC-23, CFC-115, HFC-125, among others.

- 35 A further aspect of the invention relates to using the azeotropic and azeotrope-like compositions for separating the components of the first mixture.

Brief Description Of The Drawing

Figure 1 - FIG. 1 is a schematic diagram of an extractive distillation system which can be used for practicing the process of the invention.

5       Figure 2 - FIG. 2 is a graphical representation of an azeotropic and azeotrope-like compositions consisting essentially of HCl and CFC-115 at a temperature of about -30°C.

10      Figure 3 - FIG. 3 is a graphical representation of an azeotropic and azeotrope-like compositions consisting essentially of HCl and CFC-13 at a temperature of about -20°C.

Figure 4 - FIG. 4 is a graphical representation of an azeotropic and azeotrope-like compositions consisting essentially of HCl and HFC-23 at a temperature of about -20°C.

15      Figure 5 - FIG. 5 is a graphical representation of the vapor pressure measurements in a PTx cell for a HFC-125/CFC-115 system as a function of composition at a temperature of about -10°C.

Figure 6 - FIG. 6 is a graphical representation of an azeotropic and azeotrope-like compositions consisting essentially of HFC-125 and CFC-115 at a temperature of about -50°C.

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Detailed Description

HCl and pentafluoroethane (HFC-125) in their separated and generally pure states have atmospheric pressure boiling points of about -85°C and about -49°C, respectively. However, a mixture comprising HCl and HFC-125 exhibits non-ideal vapor-liquid behavior such that the relative volatility of HCl to pentafluoroethane becomes extremely low when approaching 100% HCl purity, e.g., the relative volatility approaches 1.0. As a result, conventional distillation processes are incapable of efficiently separating pure HCl from this mixture.

30      To determine the relative volatility of HCl and a halocarbon, e.g., pentafluoroethane (HFC-125), the so-called PTx Method was used. In the PTx method, the total absolute pressure in a cell of known volume is measured at a constant temperature for various known binary compositions. Use of the PTx Method is described in greater detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on Pages 124 through 35      126; the entire disclosure of which is hereby incorporated by reference.

These measurements can be reduced to equilibrium vapor and liquid compositions in the cell by an activity coefficient equation model, such as the Non-Random, Two-Liquid (NRTL) equation, to represent liquid phase non-idealities. Use of an activity coefficient equation, such as the NRTL equation, is described in greater detail in "The Properties of Gases and Liquids, 4th edition, McGraw-Hill - publisher, Reid, Prausnitz, and Poling - Authors, pages 241 through 387; and in "Phase Equilibria in Chemical Engineering", Butterworth Publishers, 1985, Stanley M. Walas - Author, pages 165 through 244; the entire disclosure of each of the previously identified references are hereby incorporated by reference.

Without wishing to be bound by any theory or explanation, it is believed that the NRTL equation can sufficiently predict whether or not HCl and HFC-125 mixtures and/or the following other HCl and halocarbon mixtures behave in an ideal manner, and can sufficiently predict the relative volatilities of the components in such mixtures.

The results of the PTx measurements for the HCl and HFC-125 mixture at -10°C and the above series of calculations can be summarized generally in Table I below. Similar measurements were obtained and similar calculations were performed for other binary combinations of compounds which are related to the invention.

20

**TABLE I**  
**Vapor-Liquid Measurements on the HCl/HFC-125 System at -10°C**

	Mol % of HFC-125 in		Pressure psia	Relative Volatility HCl/HFC-125
	Liquid	Vapor		
25	98.43	91.29	77.8	5.980
	85.27	53.22	128.9	5.089
	73.98	39.20	163.2	4.409
	50.87	24.41	219.5	3.207
	29.88	15.75	256.5	2.280
30	19.27	11.38	271.5	1.858
	12.27	8.06	279.6	1.596
	0.00	0.00	288.0	1.172

The relative volatility of HCl in comparison to pentafluoroethane at relatively low concentrations of HCl is sufficient to permit separating HCl by using conventional distillation methods, e.g., the relative volatility at low HCl

concentrations is much greater than 1.0. However, the relative volatility approaches about 1.17 at high concentrations of HCl, e.g., when pentafluoroethane concentrations are near zero %. A relative volatility approaching 1.0 would render removal of low concentrations of HFC-125 from HCl by conventional distillation methods a costly operation requiring large and expensive distillation columns.

Even more difficult problems occur when separating relatively small quantities of chloropentafluoroethane (CFC-115), which has a boiling point at atmospheric pressure of about -39°C, from an HCl containing mixture. The results of PTx measurements and calculations for the HCl-chloropentafluoroethane system at -30°C can be summarized generally in Table II below (and shown graphically in Fig. 2 which is discussed below in greater detail).

TABLE II  
Vapor-Liquid Measurements on the HCl/CFC-115 System at -30°C

15

	Mol % of CFC-115 in		Pressure psia	Relative Volatility HCl/CFC-115
	Liquid	Vapor		
20	95.52	51.90	42.2	19.90
	80.80	23.34	90.0	13.82
	60.47	15.27	126.2	8.49
	40.64	12.02	144.1	5.01
	25.43	10.10	152.7	3.04
	10.00	6.97	157.7	1.48
25	6.99	5.76	158.5	1.23
	5.03	4.70	158.8	1.05
	3.97	4.00	158.9	0.95
	1.96	2.31	158.6	0.85

The relative volatility of HCl in comparison to chloropentafluoroethane at relatively low concentrations of HCl is sufficient to permit separating HCl by using conventional distillation methods, e.g., the relative volatility at low HCl concentrations is much greater than 1.0. However, the relative volatility drops to 1.0 at chloropentafluoroethane concentrations near about 4 mole %, thereby indicating the formation of an azeotropic or azeotrope-like composition. The formation of an azeotropic or azeotrope-like composition is also indicated by mixtures of HCl and chloropentafluoroethane which at a given temperature have a higher vapor pressure

than other mixtures as well as a higher vapor pressure than either pure component at that temperature, e.g., refer to Fig. 2. Such azeotropic or azeotrope-like formation would make it virtually impossible for conventional methods to produce HCl substantially free of chloropentafluoroethane from an HCl mixture containing 5 more than about 4 mole % chloropentafluoroethane. While conventional distillation methods may be capable of separating mixtures, which contain less than about 4 mole % chloropentafluoroethane, into the azeotropic composition and pure HCl, a significant amount of the HCl would still remain as the azeotropic or near-azeotropic mixture in proportion to the concentration of chloropentafluoroethane 10 present in the starting mixture. In addition, the relative volatility for such mixtures is sufficiently close to 1.0 that an impractically large distillation column would be required for separation.

Whenever used in the specification and appended claims the terms below are intended to have the following definitions.

15 By "azeotrope" or "azeotropic" composition is meant a constant boiling liquid admixture of two or more substances that behaves as a single substance. One way to characterize an azeotropic composition or mixture is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it was evaporated or distilled, e.g., the admixture distills/refluxes 20 without compositional change. Constant boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point, as compared with that of the non-azeotropic mixtures of the same components. An azeotropic composition can also be characterized as the maximum or minimum vapor pressure for a mixture at a given temperature when plotted as a function of 25 mole fraction.

By "azeotrope-like" composition is meant a constant boiling, or substantially constant boiling, liquid admixture of two or more substances that behaves as a single substance. One way to characterize an azeotrope-like composition is that the vapor produced by partial evaporation or distillation of the 30 liquid has substantially the same composition as the liquid from which it was evaporated or distilled, e.g., the admixture distills/refluxes without substantial compositional change. An azeotrope-like composition can also be characterized by the area, which is shown by plotting vapor pressure at given temperature as a function of mole fraction, that is adjacent to the maximum or minimum vapor 35 pressure.

Typically, a composition is azeotrope-like, if, after about 50 weight percent of the composition is removed such as by evaporation or boiling off, the change between the original composition and the composition remaining is less than about 6% and normally less than about 3% relative to the original composition.

By "effective amount" is intended to refer to the amount of each component of the inventive compositions which, when combined, results in the formation of an azeotropic or azeotrope-like composition. This definition includes the amounts of each component, which amounts may vary depending on the pressure applied to the composition so long as the azeotropic or azeotrope-like compositions continue to exist at the different pressures, but with possible different boiling points. Effective amount also includes the amounts, such as may be expressed in weight percentages, of each component of the compositions of the instant invention which form azeotropic or azeotrope-like compositions at temperatures or pressures other than as described herein. Therefore, included in this invention are azeotropic or azeotrope-like compositions consisting essentially of effective amounts of at least one of HCl or HFC-125 and at least one fluorinated molecule such that after about 50 weight percent of an original composition is evaporated or boiled off to produce a remaining composition, the change between the original composition and the remaining composition is typically no more than about 6% and normally no more than about 3% or less relative to the original composition.

It is possible to characterize, in effect, a constant boiling admixture which may appear under many guises, depending upon the conditions chosen, by any of several criteria:

25

\* The composition can be defined as an azeotrope of HCl ("A") and a halocarbon ("B"), or of HFC-125 ("C") and CFC-115 ("D"), among others, because the term "azeotrope" is at once both definitive and limitative, and requires effective amounts of A,B (or C, D) for this unique composition of matter which can be a constant boiling composition.

30

\* It is well known by those skilled in the art, that, at different pressures, the composition of a given azeotrope will vary at least to some degree, and changes in pressure will also change, at least to some degree, the boiling point temperature. Thus, an azeotrope of HCl ("A") and a halocarbon ("B") or of HFC-125 ("C") and CFC-115 ("D"), among others, represents a unique type of relationship but with a variable composition which depends on

temperature and/or pressure. Therefore, compositional ranges, rather than fixed compositions, are often used to define azeotropes.

\* The composition can be defined as a particular weight percent relationship or mole percent relationship of HCl ("A") and a fluorocarbon ("B") or of HFC-125 ("C") and CFC-115 ("D"), among others, while recognizing that such specific values point out only one particular relationship and that in actuality, a series of such relationships, represented by A,B (or C, D) actually exist for a given azeotrope, varied by the influence of pressure.

\* An azeotrope of HCl ("A") and a halocarbon ("B") or of HFC-125 ("C") and CFC-115 ("D"), among others, can be characterized by defining the compositions as an azeotrope characterized by a boiling point at a given pressure, thus giving identifying characteristics without unduly limiting the scope of the invention by a specific numerical composition, which is limited by and is only as accurate as the analytical equipment available.

The azeotrope or azeotrope-like compositions of the present invention may be formed by operating a conventional distillation apparatus, when practicing the inventive extractive distillation method, and by combining effective amounts of the components by any convenient method including mixing, combining, among others. For best results, a preferred method is to weigh the desired component amounts, and thereafter combine them in an appropriate container.

HCl and chlorotrifluoromethane (CFC-13) may form an azeotropic composition consisting essentially of about 37 mole % chlorotrifluoromethane and about 63 mole % HCl with a pressure of about 277 psia when at a temperature of about -20°C, e.g., refer to Figure 3 which is discussed below in greater detail. Conventional distillation methods would be expected to produce a separated mixture wherein a significant portion of the HCl remains in the azeotropic or azeotrope-like mixture. In addition, the relative volatility for such mixtures is sufficiently close to 1.0 that an impractically large distillation column would be required for separation.

HCl and trifluoromethane (HFC-23) may also form an azeotropic composition consisting essentially of about 45 mole % trifluoromethane and about 55 mole % HCl with a pressure of about 262 psia when at a temperature of about -20°C, e.g., refer to Figure 4 which is discussed below in greater detail. Conventional distillation methods would be expected to produce a separated mixture wherein a significant portion of the HCl remains in the azeotropic or azeotropic-like mixture.

## 10

In addition, the relative volatility for such mixtures is sufficiently close to 1.0 that an impractically large distillation column would be required for separation.

The problems associated with conventional distillation methods are overcome in the present invention by using an extractive distillation method.

5 Extractive distillation depends upon the ability of certain extractive agents to increase the relative volatility of the compounds to be separated. Extractive distillation is typically performed by operating a continuous distillation column, which comprises a multi-stage distillation column, with a minimum of two feed points, e.g., introducing the extractive agent at a first feed point which is located  
10 above the second feed point that is used for introducing the mixture to be separated, a reboiler and an overhead condenser for returning reflux to the column.

Given the relative volatilities of HFC-125, CFC-115, CFC-13, HFC-23 and HCl, it was a surprising and an unexpected result that using an extractive distillation process can purify or separate HCl. It was a particularly surprising and  
15 an unexpected result that the inventive process is capable of separating HCl from mixtures containing HFC-125 and HCl, CFC-115 and HCl, CFC-13 and HCl, or HFC-23 and HCl; wherein at least 99.0 % of the HCl is recovered and the recovered HCl has at least about 99.99 % by weight purity.

In one aspect of the invention, an extractive agent, e.g., 2-chloro-  
20 1,1,1,2-tetrafluoroethane (HCFC-124), is introduced at an upper feed point of the distillation column, whereas the mixture requiring separation, e.g. HCl and pentafluoroethane, is introduced at a relatively lower feed point of the column. The liquid extractive agent passes downwardly through trays which are located in the center of the column. While in the presence of the extractive agent, HCl is  
25 relatively more volatile than the halocarbon, thereby allowing HCl, which is substantially free from the halocarbon, to escape from the top of the column. The liberated HCl is condensed using known techniques, e.g., the HCl is condensed using conventional reflux condensers. At least a portion of this condensed HCl stream can be returned to the top of the column as reflux, and the remainder  
30 recovered as a useful product. The ratio of the condensed material, which is returned to the column, to the material removed as product is commonly referred to as the reflux ratio. The halocarbon and extractive agent exiting the column can then be passed to a stripper or distillation column for separation by using conventional distillation or other known methods and, if desired, recycle of the extractive agent to  
35 the extractive distillation column.